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Tar property, analysis, reforming mechanism and model for biomass gasification—An overview

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Abstract

Biomass becomes an important primary energy source as well as renewable energy source. As the most promising biomass utilization method, biomass gasification is gaining attention as a route for biomass energy production, but producer gas from this process usually contains unacceptable levels of tar. The tar control and convert is a key issue for a successful application of biomass-derived producer gas. A detail overview on tar chemical and physical properties, reforming mechanism and reaction kinetic model are summarized in this paper.

Keywords: Biomass tar; Property; Analysis; Technology; Reaction mechanism; Model

Contents

1. Introduction

With the depletion of fossil fuel sources as well as the global warming issues, the utilization of biomass is getting increased attention as a potential source of renewable energy. At present, biomass share in the world's total primary energy consumption is about 12%, it is estimated that biomass share will be increased to near 15% by 2010 in developed countries [1].

Biomass fuels and residues can be converted to energy via thermal, biological and physical processes. Each process area is described with the greatest emphasis on the technologies that are attracting the most attention in the research, demonstration and commercial arenas. Thermo-chemical conversion covers

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different processes combustion, gasification and pyrolysis with interleaved boundaries.

Biomass gasification is gaining attention as a route for biomass energy production, but producer gas from this process usually contains unacceptable levels of tar. Tar can cause operational problems in downstream processes by blocking gas coolers, filter elements and engine suction channels. Most producer gas applications also require removal of at least part of the dust and tar before the gas can be used. Hence, the tar control and convert is a key issue for a successful application of biomass-derived producer gas.

2. Definition and composition of tar

As the formula (1) shows, the product gas formed from biomass gasification contains the major components CO, H_2, CO_2, CH_4, H_2O, and N_2, in addition to organic (tars) and inorganic (H_2S, HCl, NH_3, alkali metals) impurities and particulates. The organic impurities range from low molecular weight hydrocarbons to high molecular weight polynuclear aromatic hydrocarbons. The lower molecular weight hydrocarbons can be used as fuel in gas turbine or engine applications, but are undesirable products in fuel cell applications and methanol synthesis. The higher molecular weight hydrocarbons are collectively known as ‘‘tar’’. These tars tend to be refractory and are difficult to remove by thermal, catalytic or physical processes. And also tar can condense or polymerize into more complex structures in exit pipes, heat exchangers or on particulate filters, leading to choking and attrition, which can result in decrease of total efficiency and a increase in the cost of the process. So the aspect of tar cracking or removal in gas clean-up is one of the most important technical uncertainties in implementation of gasification technologies and is discussed below:

$$\begin{aligned} \text{biomass} + O_2(\text{or } H_2O) \quad &\rightarrow \quad CO,\ CO_2, H_2O, H_2,\ CH_4 + \text{other hydrocarbons} \\ &\rightarrow \quad \text{tar} + \text{char} + \text{ash} \\ &\rightarrow \quad HCN + NH_3 + HCl + H_2S + \text{other sulfur gases} \end{aligned} \tag{1}$$

2.1. Definition and composition of tar

One of the issues associated with biomass gasifier tars is how they are defined. More often than not, tar is given an operational definition by that conducting biomass gasification R&D. An excellent report by Milne et al. [2] describes in detail the operational definitions of biomass gasification tars as published in the literature and provides a comprehensive survey of tar formation and conversion. It is not the intent of this report to provide the definition of ‘‘tars’’ but, for the most part, ‘‘tars’’ are considered to be the condensable fraction of the organic gasification products and are largely aromatic hydrocarbons, including benzene. The diversity in the operational definitions of ‘‘tars’’ usually comes from the variable product gas compositions required for a particular end-use application and how the ‘‘tars’’ are collected and analyzed. Tar sampling protocols are being developed to help standardize the way tars are collected [3]; however, these methods are not yet widely established. Regardless of how ‘‘tar’’ is defined, tar removal, conversion, or destruction is seen as one of the greatest technical challenges to overcome for the successful development of commercial advanced gasification technologies.

Tars are formed during gasification in a series of complex reactions. The formation of tar is highly dependent on the reaction conditions. Due to increased reaction temperature, secondary reactions occur in the gas phase which convert oxygenated tar compounds to light hydrocarbons, aromatics, oxygenates and olefins subsequently forming higher hydrocarbons and larger PAH in tertiary processes [4].

The tar formation scheme proposed by Elliott and summarized by Milne [2] is presented in Fig. 1, Elliott [5] reviewed the composition of biomass pyrolysis products and gasifier tars from various processes. Fig. 1 shows the transition as a function of process temperature from primary products to phenolic compounds to aromatic hydrocarbons, and Table 1 shows the classes of chemical components in each major regime based on GC/MS analysis of collected ‘‘tars.’’

In a later publication, Baker et al. [6] showed a conceptual relationship between the yield of ‘‘tars’’ and the reaction temperature as shown in Fig. 2. They cited levels of ‘‘tar’’ for various reactors with updraft gasifiers having 12 wt% of wood and downdraft less than 1%. Steam-blown, fluid-bed gasifiers had tar levels of 15% at 600 °C and 4% at 750 °C. For oxygen-blown fluid-bed, the levels of ‘‘tar’’ were 4.3% at 750 °C and 1.5% at 810 °C. The entrained flow gasifier of Battelle Columbus Laboratories, operated at 1000 °C, had ‘‘tar’’ levels of 1%. Table 2 tabulates the variety of reported levels of ‘‘tar.’’

For the tar element composition, not enough data were found to establish a relationship with temperature. The carbon, hydrogen and oxygen contents in tar do not seem to vary with temperature, but only a sample of four species with just few points was available as a support for this judgement. The mass percentage of carbon in tar remains approximately at 54.5%, the percentage of hydrogen at 6.5% and the percentage of

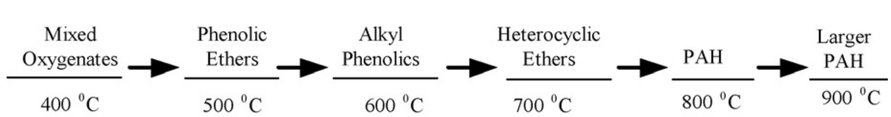


Fig. 1. Tar maturation scheme proposed by Elliott [5].

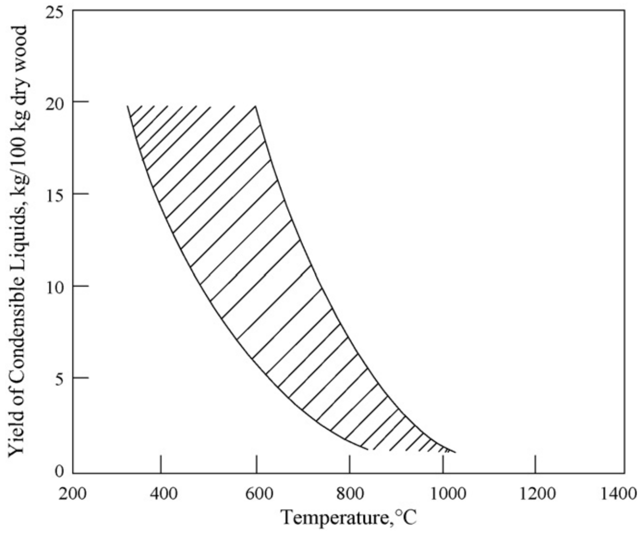


Fig. 2. "Tar" yield as a function of the maximum temperature exposure (Baker et al. [6]).

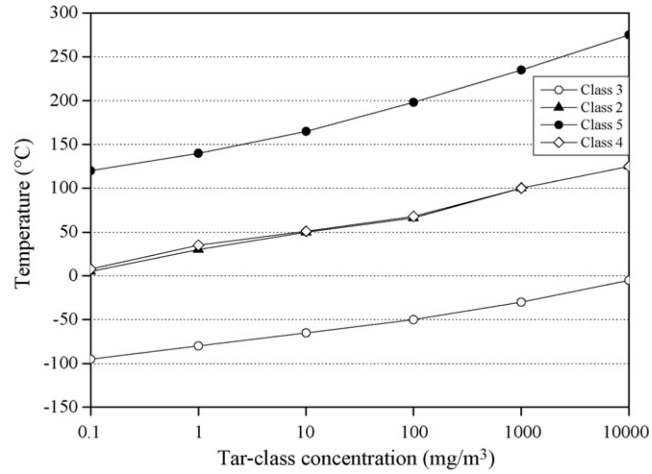


Fig. 3. The tar dewpoint of the different tar classes in relation to the concentration.

oxygen was about 39%. These values can be considered as approximations of carbon, hydrogen and oxygen contents in tar [7].

2.2. Tar chemical and physical properties

Tar is a complex mixture of condensable hydrocarbons, which includes single ring to 5-ring aromatic compounds along with other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbon (PAH). Various research groups are defining tar differently. In the EU/IEA/US-DOE meeting on tar measurement protocol held in Brussels in the year 1998, it was agreed by a number of experts to define tar as all organic contaminants with a molecular weight larger than benzene [8].

2.2.1. Tar classes

Based on the molecular weight of tar compounds, some researchers [9,10] divided tar components into five groups, as shown in Table 1.

Tar leads to fouling once the gas becomes (over) saturated with it. This leads to aerosol formation and depositions inside the installation. These fouling phenomena are not of concern as long as all the tar is present in the gas phase. It is therefore believed that the tar problem is fundamentally not concerned with the tar quantity, but is with the properties and the composition of the tar.

Table 1
List of tar compounds that are considered for different tar classes

Tar class	Class name	Property	Representative compounds
1	GC-undetectable	Very heavy tars, cannot be detected by GC	Determined by subtracting the GC-detectable tar fraction from the total gravimetric tar
2	Heterocyclic aromatics	Tars containing hetero atoms; highly water soluble compounds	Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol
3	Light aromatic (1 ring)	Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility	Toluene, ethylbenzene, xylenes, styrene
4	Light PAH compounds (2–3 rings)	2 and 3 rings compounds; condense at low temperature even at very low concentration	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
5	Heavy PAH compounds (4–7 rings)	Larger than 3-ring, these components condense at high-temperatures at low concentrations	Fluoranthene, pyrene, chrysene, perylene, coronene

Table 2
Chemical components in biomass tars

Conventional flash pyrolysis (450–500 °C)	Acids aldehydes ketones furans alcohols complex oxygenates phenols guaiacols syringols complex phenols
High-temperature flash pyrolysis (600–650 °C)	Benzenes phenols catechols naphthalenes biphenyls phenanthrenes benzofurans benzaldehydes
Conventional steam gasification (700–800 °C)	Naphthalenes acenaphthylenes fluorenes phenanthrenes benzaldehydes phenols naphthofurans benzanthracenes
High-temperature steam gasification (900–1000 °C)	Naphthalene acenaphthylene phenanthrene fluoranthene pyrene acephenanthrylene benzanthracenes benzopyrenes 226 MW PAHs 276 MW PAHs

The condensation behaviour of tar is an integral effect of all tar components that are present in the syngas. The components their individual contribution to the total tar vapour pressure is there in decisive. When the tar vapour pressure exceeds the saturation pressure of the tar, the gas becomes (over) saturated according Raoult's Law [11]. Thermodynamically, this state leads to condensation of the saturated vapour. The tar dewpoint is the temperature at which the real total partial pressure of tar equals the saturation pressure of tar. Hence, in condensation related issues, the tar dewpoint is a powerful parameter to evaluate the performance of gas cleaning systems. It is believed that, when the dewpoint of tar is reduced to levels below the lowest expected temperature, fouling related problems by condensation or tar aerosols are solved. To use this approach in design issues, a calculation tool has been developed to predict the tar dewpoint on basis of the concentration of the individual tar components in the syngas. An illustration of the relation between the tar dewpoint and tar concentration is summarized by Bergman [12] and shown in Fig. 3. Condensation curves are given for the individual tar classes, e.g. the dewpoint curve for class 5 is calculated including only class 5 tars. Furthermore, each tar component is contributes equal to the total concentration on mass basis. The dewpoint calculation excludes tar class 1, as the components are not known. For a CFB gasifier it is believed that tars that belong to class 1 start to condense around 300–350 °C [12].

Even at low class 5 tar concentration of circa 0.1 mg/m^3, the corresponding dewpoint (°C) exceeds the dewpoint valid for high concentration of class 2, 3, and class 4 tar (e.g. 1000 mg/m^3).

It can be derived from Fig. 3 that class 5 tars dominate the dewpoint of tar. Even for very low concentrations of class 5 tars (e.g. <1 mg/m^3) a dewpoint below 100 °C can be obtained. The graph clearly points out that, dependent on the concentration in the syngas, classes 2 and 4 need to be partially removed for a proper tar dewpoint of about 25 °C. The class 3 tar compounds do not condense at concentration as high as 10,000 mg/m^3, and play an unimportant role in this matter.

2.2.2. Tar heat enthalpy and entropy

Evaluation of the thermodynamic properties of tar is important in the development and analysis of biomass or coal related processes as gasification, liquefaction, pyrolysis. Specifically, the evaluation of the enthalpy and entropy of these compounds is essential for performing first and second law analyses. Until now several studies have been made on the specific heat, enthalpy, and entropy of tar. Eisermann proposed one method for evaluating the specific heat, enthalpy, and entropy of tar [13].

Hyman and Kay [14] proposed one correlation formula for the specific heat of the tar produced in the gasification of coal:

$$C_T = \frac{1}{D}(4.94 \times 10^{-3} T) \quad (2)$$

where C_T is the specific heat (kJ/kg tar K), D the specific gravity at 289 K/289 K and T is the temperature (K).

For the formula, Lowry [15] proposed that using a typical specific gravity value of 1.17, the equation can be rearranged to give:

$$C_T = 4.22 \times 10^{-3} T \quad (2)$$

standard enthalpy of tar.

Tar produced from different resource, the results is different, for example, two widely different coals (a Pittsburgh seam and a Wyodak seam) have been given a heat content value of 130,000 BTU per gallon. Eisermann et al. [13] proposed the following equation for the enthalpy and entropy:

$$\begin{aligned} H = H^\circ + \int C_T \, dT, \quad H^\circ \\ = -\Delta H^\circ + \eta_C H^\circ_{CO_2} + \eta_S H^\circ_{SO_2} + \frac{\eta_H}{2} H^\circ_{H_2O}, \quad \Delta H^\circ \\ = 30.980\,\text{kJ/kg tar}, \; S = S^\circ + \int \frac{C_T}{T} \, dT, \; S^\circ \\ = a_1 + a_2 \exp\left(- a_3 \left(\frac{H}{C} + N \right) \right) + a_4 \left(\frac{O}{C+N} \right) \\ + a_5 \left(\frac{N}{C+N} \right) + a_6 \left(\frac{S}{C+N} \right) \end{aligned}$$

where S° is the standard entropy (kJ/kmol carbon K), $a_1 = 37.1635$, $a_2 = -31.4767$, $a_3 = 0.564682$, $a_4 = 20.1145$, $a_5 = 54.3111$, and $a_6 = 44.6712$.

Thunman [7] proposed the another formula of heating value of tar. A general assumption for the heating value of tar is that the composition of tar is close to that of wood between 673 and 923 K, so the heating value of tar is between 22 and 26 MJ/kg (combustible substance), and between 973 and 1273 K, the composition is close to that of lumped hydrocarbons, whose heating value is about 40 MJ/kg. However, no further data were found to make a model. So, initially, it was thought that the heating value of tar could be determined from the heating value of its components, but the different substances present in tar and their amount were too difficult to find. Finally, a general correlation of Mason and Gandhi [16] was adopted:

$$\text{HHV} = 146.58 X_{C,tar} + 568.78 X_{H,tar} - 51.53 X_{O,tar}$$

where HHV is the high heating value, is expressed in Btu/lb. As 1 Btu/lb = 2.326 kJ/kg, it becomes in kJ/kg: HHV = 340.95 $X_{C,tar}$ + 1322.98 $X_{H,tar}$ − 119.86 $X_{O,tar}$.

3. Tar analysis

During the past decades, several institutes have developed methods for the sampling and analysis of tars, on-line and off-line. The sampling part of the off-line methods is based on trapping the tar by condensation on cold surfaces or filters, by absorption in a cold organic solvent or by adsorption on a suitable sorbents. The analysis of the tars is most often performed by gas chromatography (GC) or gravimetrically (by weighing the collected tars, after careful evaporation of the solvent and condensed water). The latter method has been used for over a decade in the framework of the worldwide UNDP/

World Bank monitoring program. Recently, on-line methods have been developed and improvements of these methods are being further investigated. Among these methods, the European tar protocol is the most popular and accepted by researchers.

3.1. European tar protocol

The members of the Gasification Task of the IEA Bioenergy Agreement, the US DoE and DGXVII of the European Commission have been aware of the diversity of methods and definitions for organic contaminants and of the resulting problems. To address it they called a joint meeting in Brussels, March 1998, where it was decided to develop two sampling and analysis Protocols that could be used as reference methods for further work. One Protocol would be used for small scale, fixed bed, engine-based systems and the other for larger utility scale plants. The two draft Protocols were discussed in a workshop at the 10th European Biomass Conference in Würzburg and will further be referred to as 'Würzburg Protocols'. In order to further develop the Würzburg Protocols to widely accepted and standardised Protocols and to integrate them to one Protocol, the EU fifth framework project 'Tar Protocol' has been submitted. It was accepted and has started per April 1, 2000. 17 Partners participate in the project, of which 7 are contractors and 10 reviewers [3,17,18].

The guideline, which was developed in a previous EU project, provides a set of procedures for the measurement of organic contaminants and particles in producer gases from biomass gasifiers. The procedures are designed to cover different air or oxygen-blown gasifier types (updraft or downdraft/fixed bed or fluidized bed gasifier), operating conditions (0–900 °C and 0.6–60 bars), and concentration ranges (1–300 mg/m^3). This procedure includes four parts gas preconditioning (atmospheric gasifiers and pressurized gasifiers), particle filter, tar collection, volume metering, after handling by the four parts, the clean tar is collect in isopropanol, then be analyzed by GC, which is shown in Fig. 4.

Collection of moisture and tar is performed in a series of 6 impinger bottles or in specially designed equipment referred to as ''Petersen column''. The sampling principle and equipment of these two equipments (6 impinger bottles and Petersen column) are shown in Fig. 4.

In the series of impinger bottles, the first impinger bottle acts as moisture collector, in which water and tar condensed from the process gas by absorption in isopropanol. The heat released by gas cooling and condensation is removed either in an external water bath or by an additional heat exchanger before the condenser. The heat exchanger may be necessary for high moisture producer gases (e.g. from steam gasification) and should be designed to meet the demands of the gasifier.

The condenser is a standard impinger bottle or can optionally be equipped with an internal liquid quench system which is especially suitable for producer gases containing higher tar levels. When using a liquid quench, isopropanol is the circulating liquid. After the moisture collector the gas is passed through a series of 4 impingers with solvent and 1 final impinger which is empty. Direct condensation of the liquid effluent without diluting media, e.g. with cold trapping, can result in further reaction of the trapped compounds. Fine-meshed frits give better results than coarse-meshed frits; G3 frits should be installed in the impinger train. If G3 frits give a too high a pressure drop (e.g. 0.5 bar), G2 frits should be used.

Petersen column is an alternative equipment for the 6 impinger bottles in Fig. 4, which consists of two washing stages filled with isopropanol. It is jacket cooled. The cooling fluid and cooling temperature can be selected as required.

Gas chromatograph is the main analysis apparatus, which is (or should be) fitted with a capillary column, a flame ionization detector and a data processing system. The stationary phase of the capillary column should be bonded poly(5%diphenyl/95%dimethylsiloxane). The recommended dimensions are an

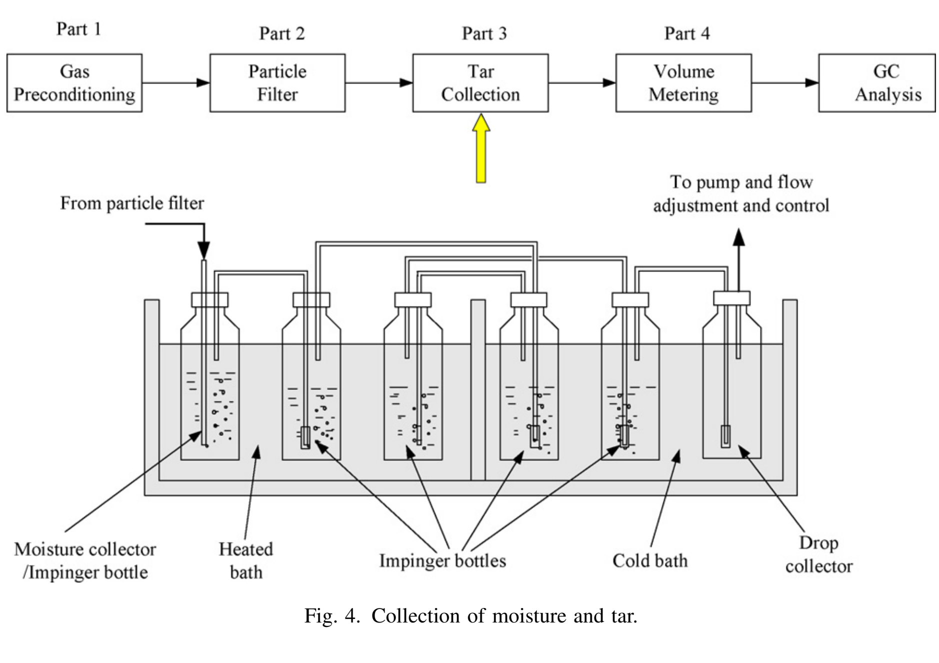


Fig. 4. Collection of moisture and tar.

internal diameter of 0.25–0.32 mm and a length of 30–60 m. It should be noted that this length is suited to the defining of total GC-tar but for determining individual compounds the length is suited to the defining of total GC-tar but for determining individual compounds the length maybe to short. The typical gas chromatograph parameters are: column temperature program: 50 °C for 5 min. To 325 °C at 8 °C/min, stop for 5 min; injector: split, 1:75; injector temperature: 275 °C; detector temperature: 300 °C; injection volume: 1–2 μl; carrier gas: hydrogen or helium, column pressure adjusted so that the linear velocity of hydrogen is 30–55 cm/s and helium 20–40 cm/s.

The result of the analysis depends on the response factor of the compounds used for calibration. Naphthalene is selected for the external calibration procedure, and *o*-Terphenyl as the internal standard, the detail explanation please find Refs. [19,20].

3.2. Other methods

Buck scientific analysis the Naphthenes and cal tars with GC–PID. Photo-ionization detectors are much more sensitive than the conventional TCD or FID, and have the added benefit of an extremely strong response to olefins and aromatics over saturated compounds in the coal tar distillate. However, TCD's and FID's are usually far less expensive to purchase. This leaves many plants with a limited resource for gathering data on their distillation process. Instrumentation: Buck 910GC, Column: Mxt-5; 30 m × 0.53 mm I.D. × 0.50 μm, detectors: photo-ionization (PID), injectors: heated split/splitless; 250 °C, carrier gas: helium at 20 cm/s, oven program: 60–350 °C at 10 °C/min [21].

Aygun et al. [22] developed an extraction method for benzo[*a*]pyrene determination. The benzo[*a*]pyrene identification and quantification were carried out by means of high-pressure liquid chromatography.

Alben [23] analyzed samples of leachate from a commercial coal for polycyclic aromatic hydrocarbons (PAHs) by capillary gas chromatography–mass spectrometry, using electron impact and chemical ionization. Bas neutral extracts Contained predominantly the parent PAHs and alkyl- and nitrogen-substituted PAHs. These compounds were considerably less abundant in samples of chlorinated leachate, which contained, instead, a number of oxygenated and halogenated PAHs.

Zhang et al. [24] developed one high performance liquid chromatography (HPLC) method, systematic study was made on the identification and quantitative determination of PAHs in heavy products derived from coal and petroleum with HPLC. After the separation of PAHs by a high-resolution column, identification was made through four methods: (1) the relative retention time (RRT) method, (2) the stop-flow-UV scanning method, (3) the method of fluorescence characteristic index Φ' and (4) the method of V' index at different UV wavelengths. For the quantitative determination of the components, methods of external standard (E-X), internal standard (I-N) and external standard-response factors (E-F) were compared in this paper. He suggested the E-F method. For the determination of quantitative response factors (F) two methods were studied, including the HPLC peak-area method (Peak-area method) and the UV absorbance method using a UV spectrometer (absorbance method). The absorbance method was better and is recommended in the paper, and the F values of 30 PAHs from the two different methods are given. Lastly, a coal tar pitch, a thermal cracking residue oil and a residual oil from ethylene production are analyzed by the method.

Karellas and Karl [25] developed one optical measurement system based on laser spectroscopy. This system can measure not only the basic components of the product gas (H_2, CH_4, CO, CO_2, H_2O), but it also gives information concerning the content of high hydrocarbons, the so-called tars, in the product gas. But the analysis system usually used in low tar process.

4. Reaction mechanism and kinetic

Tar decomposition mainly occurs due to cracking, steam and dry reforming reactions as shown below [26].

Cracking: $pC_nH_x \rightarrow qC_mH_y + rH_2$.
Stream reforming: $C_nH_x + nH_2O \rightarrow (n + x/2)H_2 + nCO$.
Dry reforming: $C_nH_x + nCO_2 \rightarrow (x/2)H_2 + 2nCO$.
Carbon formation: $C_nH_x \rightarrow nC+(x/2)H_2$.
C_nH_x represents tar, and C_mH_y represents hydrocarbon with smaller carbon number than C_nH_x.

4.1. Decomposition mechanism

After analysis of experimental results, Jess [27] presented the reaction scheme of thermal conversion of tar (aromatic hydrocarbons) in the presence of H_2 and H_2O, and shown in Fig. 5. From which, it is can conclude that benzene is the key component of thermal decomposition of tar (aromatic hydrocarbons), and a carbonaceous residue (soot) is formed, above all from naphthalene. The soot as well as the organic cracking products (e.g. methane) primarily formed react with H_2O in consecutive reaction steps. He also pointed that the thermal conversion of aromatic hydrocarbons in product gases from pyrolysis and gasification of solid fuels, temperatures of ~1200 °C are necessary at residence times of technical relevance (<10 s). To convert the soot and organic cracking products primarily formed to CO and H_2, even higher temperatures of at least 1400 °C are required.

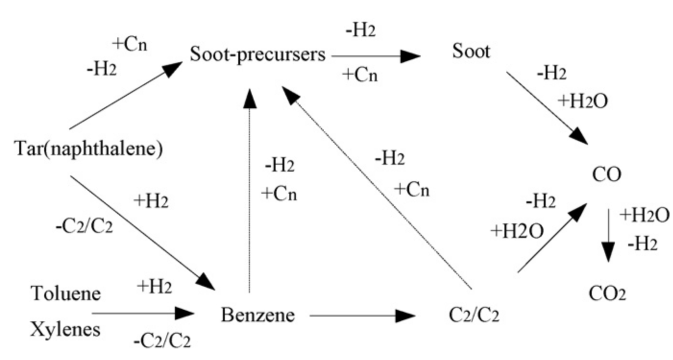


Fig. 5. Simplified reaction scheme of thermal conversion of aromatic hydrocarbons the presence of hydrogen and steam.

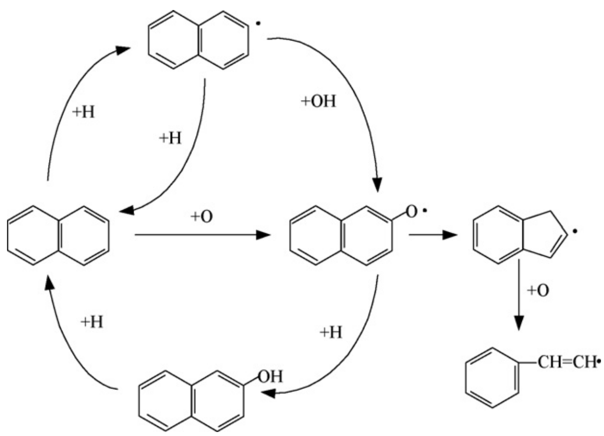


Fig. 6. Naphthalene decomposition scheme.

Nair et al. [28] proposed naphthalene decomposition scheme by Pulsed Corona method, and shown in Fig. 6, which is proposed according to the product distribution observed during experiments. Byproducts were mainly formed by an oxidation mechanism. Intermediate compounds seen in Fig. 6 lead to byproduct formation of naphthalene-dione and phthalicanhydride, which was observed by GC/MS analysis, as well. The main path for ring opening is via naphthoxy formation and its decomposition to indenyl via a thermal mechanism, which largely governs the decomposition scheme. After analysis and discussion, he proposed the complete scheme for corona processing in a fuel gas mixture as shown in Fig. 7.

Frederick and co-workers [29] proposed unimolecular and bimolecular decomposition mechanism for tar transformations, and give a example, unimolecular reactions and bimolecular decomposition of vanillin, shown in Figs. 8 and 9.

4.2. Reaction kinetic

4.2.1. Model component

Because of the complexity of tar, several researchers have studied these decomposition reactions using model biomass tar compounds such as phenol, toluene, 1-methyl-naphthalene,

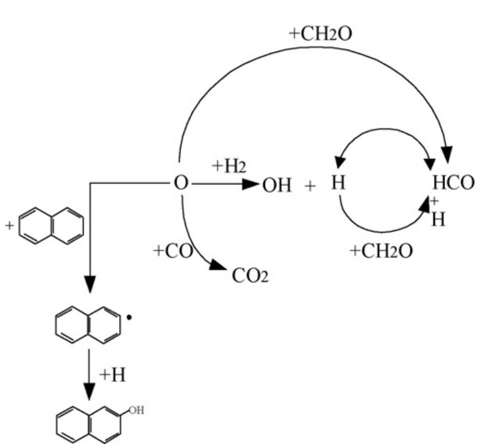


Fig. 7. Main reaction pathways for reactive radicals in corona processing of fuel gas for naphthalene removal at 200 °C.

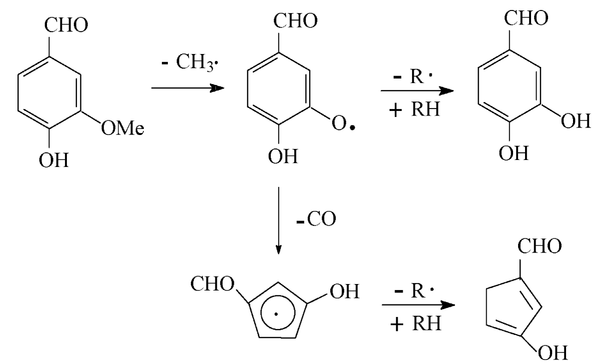


Fig. 8. Unimolecular reactions of vanillin.

naphthalene and so on. The general reaction kinetic equations used are shown in the following:

$$-r_{\mathrm{tar}} = k_{\mathrm{app}}C_{\mathrm{tar}}, \quad k_{\mathrm{app}} = \frac{[-\ln(1-X)]}{\tau}, \quad \tau = \frac{W}{v_0}, \quad k_{\mathrm{app}} = k_{0,\mathrm{app}}e^{(-E_{\mathrm{app}}/RT)}.$$

Devi et al. [26] used naphthalene component as the tar model, the catalytic activity of olivine is investigated via steam-reforming. During dry reforming reaction with CO_2, naphthalene conversion of about 80% is observed and both steam and dry reforming reaction of naphthalene forms more than 50% gaseous products over 10 h pretreated olivine. The apparent rate constant and the apparent activation energy for naphthalene decomposition over 10 h pretreated olivine under syngas mixture is calculated assuming a first-order reaction with respect to naphthalene. The temperature dependency is calculated according to Arrhenius' Las, apparent activation energy for naphthalene conversion over 10 h pretreated olivine calculated is 187 kJ mol^{-1} with frequency factor of 2.06×10^9 $m^3\ kg^{-1}\ h^{-1}$.

Jess [27] use naphthalene, toluene and benzene as aromatic hydrocarbon. The kinetics of the thermal conversion in the presence of hydrogen and steam were studied. The experiments were performed in a tubular flow reactor at a total pressure of 160 kPa, temperatures of 700–1400 °C, residence times of 0.3–2 s and different gas-phase concentrations of hydrogen, steam and the aromatics. The mechanisms of primary and consecutive reactions are presented as reaction schemes that are supported by kinetic calculations. The following order of reactivity is obtained: toluene $\gg$ naphthalene $>$ benzene. Besides gaseous organic cracking products such as methane and ethane, condensed products and a carbonaceous residue (soot) is formed, principally from naphthalene. Soot formation is strongly inhibited by hydrogen. Steam has only a little influence on the conversion of the aromatics. Under the given reaction conditions, neither the soot primarily formed nor the organic cracking products such as methane are completely converted by steam to carbon monoxide and hydrogen, even at the highest temperature. He proposed reaction mechanism of naphthalene, toluene and benzene shown in Fig. 5. The reaction condition and results of kinetic data of thermal conversion are shown in Tables 3 and 4 respectively.

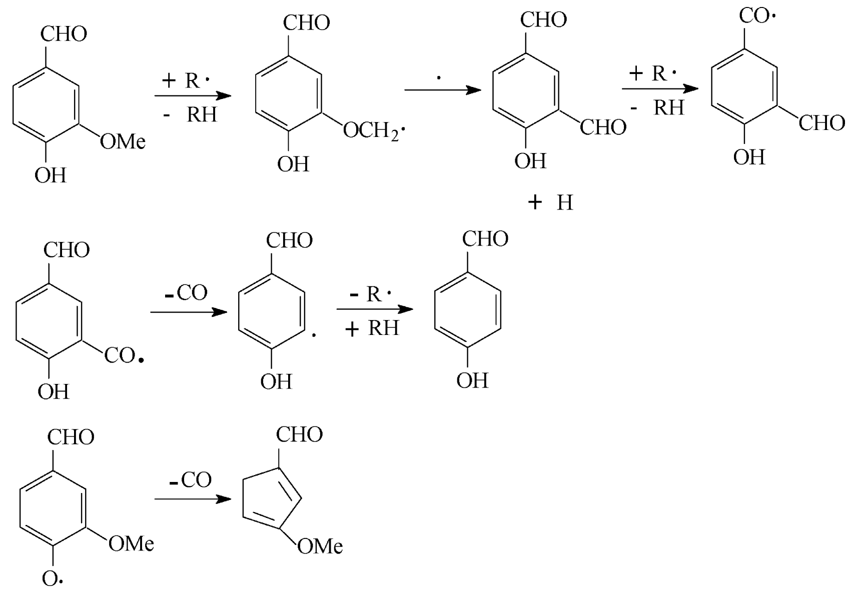


Fig. 9. Bimolecular decomposition of vanillin.

Swierczynski et al. [30,31] use toluene as model component of tar. A model study in laboratory scale fixed bed reactor of toluene steam-reforming is studied, the toluene conversion obtained with Ni/olivine at 560 °C is the same as with olivine at 850 °C. A kinetic model established, taking into consideration a zero order for water and first-order for toluene gives the kinetic parameters ($E_a = 196$ kJ mol^{-1} and $A(k') = 3.14 \times 10^{13}$ m^3 (kg$_{cat}$ h)$^{-1}$) comparable to those reported for steam-reforming of benzene or tars on commercial nickel catalysts.

In this study, the reactor has been considered as plug flow with no gas expansion (constant flow rate through it). We have assumed that the power-law type general equation $-r_t = kc_t^n c_{H_2O}^m$ for the disappearance rate of tar in a binary reaction with H_2O can be expressed as a pseudo-order reaction with respect to only toluene concentration $-r_t = k'(H_2O)c_t^n$. The decomposition rate of tar can be assumed to be first-order. The first-order rate constants can then be calculated derived from an integral plug flow reactor model.

The temperature dependence on the rate constant is determined by the Arrhenius equation, from which the activation energy and pre-exponential factor of the rate constant can be calculated and shown in Table 5.

Taralas et al. [32] used toluene as model component of tar. Thermal destruction of vaporized toluene in the presence of a [$N_2 + H_2O + O_2$] in air and [$N_2 + H_2 + H_2O$] gas mixtures are examined. Experiments were performed in a non-isothermal tubular flow reactor at a total pressure of ca. 101.3 kPa, temperature range of 973–1223 K. In presence of oxygen-containing molecules (molar ratios of [$H_2O + O_2$]/C_7H_8 were varied between 1.78 and 3.52), a first-order reaction rate could express the effects of temperature and residence time. Thermal destruction of toluene in [$N_2 + H_2 + H_2O$] gas mixture ([$H_2 + H_2O$]/C_7H_8) 3.52, and ($0.40 < \tau < 0.90$ s) was studied

Table 3
Reaction conditions of experiments (standard conditions in brackets; total pressure 160 kPa)

	Content (vol.%) (rest nitrogen)			Residence time at 1100 °C (s)	Temperature T_R (°C)
	Hydrocarbon	Hydrogen	Steam		
Benzene	0.3–1.2 (0.6)	0–76 (40)	0–40 (20)	0.5–1 (0.5)	800–1400
Toluene	0.6	20–40 (40)	20	1	700–1400
Naphthalene	0.25–1 (0.5)	0–48 (48)	0–32 (20)	0.3–2 (0.5)	950–1400

Table 4
Kinetic data of thermal conversion of naphthalene, toluene and benzene

Hydrocarbon	Pre-exponential factor	Activation energy (kJ mol^{-1})	Reaction order		
			Hydrocarbon	Hydrogen	Steam
Naphthalene	1.7×10^{14} m$^{0.3}$ mol$^{-0.1}$ s^{-1}	350	1.6	−0.5	0
Toluene	3.3×10^{10} m$^{1.5}$ s^{-1}	247	1[a]	0.5	0[a]
Benzene	2.0×10^{16} mol$^{0.1}$ m$^{-0.3}$ s^{-1}	443	1.3	−0.4	0.2

[a] Assumption of first-order reaction with respect to toluene and zero-order reaction with respect to steam.

Table 5
Estimates of the kinetic parameters for the first-order toluene decomposition rate on Ni/olivine catalyst

Parameter	Estimated value
$k'(T_r)$ (m^3 $(kg_{cat}\ h)^{-1}$)	1896 (800 °C)
$A(k')$ (m^3 $(kg_{cat}\ h)^{-1}$)	3.14×10^{13}
E_a (kJ mol^{-1})	196

as reference. Activation energies of the thermal destruction of toluene are: 356 ± 5 kJ mol^{-1} in $[N_2 + H_2O + O_2]$ atmosphere, $2.3 \times 10^{15}\ s^{-1}$ the frequency factor.

The temperature dependence ($1098 < T < 1223$ K) of the rate constant for overall hydrodealkylation reaction $C_7H_8(g) + H_2(g) \rightarrow C_6H_6(g) + CH_4(g)$ $-\Delta H_{r(1173\ K)} = 101$ kJ mol^{-1} was determined. The rate constant was calculated from the toluene conversation at different temperatures and as plotted according to the Arrhenius law, the calculated activation energy E is 250 ± 10 kJ mol^{-1} in $[N_2 + H_2 + H_2O]$ gas mixture and the frequency factor $3.3 \times 10^{10}\ mol^{-0.5}\ m^{1.5}\ s^{-1}$. A chemical reaction network and a free-radical mechanism have been suggested to explain the products concentration distribution. The free-radical mechanism has been used to interpret the experimental trends at gas residence times ($\tau < 5$ s).

Simell and Hirvensalo [33] used benzene as model component of tar. The reactions of the gas main components were included in the models studied. Kinetic studies were carried out at 750–925 °C and under ambient pressure in a plug flow reactor using a mixture of simulated gasification gas. Operation conditions without external or internal mass-transfer limitations were applied. Mechanistic models of the Langmuir–Hinshelwood type describing benzene decomposition were developed and tested, and shown in Table 6. Experimental results could be best described by a kinetic rate equation based on the assumption that single site adsorption of benzene was the rate-determining step and that adsorption of hydrogen inhibited benzene decomposition.

Dou et al. [34] chose 1-methylnaphthalene as a model of tar component. Five catalysts were evaluated to tar component removal from high-temperature fuel gas in a fixed-bed reactor. The Y-zeolite and NiMo catalysts were found to be the most effective catalysts. Two catalysts almost removed 100% tar component at 550 °C. The process variables, temperature and space velocity, have very significant effects on tar component removal with catalysts. The long-term durability shows that two catalysts maintain more than 95% removal conversion at 550 °C in 168 h. The combustion study of coke deposited on catalysts by thermal gravimetric analysis technology shows that very small amount build up of coke appears on two catalysts surface. Using a first-order kinetic model, the apparent energies of activation and pre-exponential factors for tar component removal reaction and coke combustion on catalysts were obtained for the most active catalysts. He assume the reaction as first-order (for tar) kinetic equation, and obtained apparent activation energies around 66.6 and 37.2 kJ/mol for NiMo and Y-zeolite, respectively. The k_0 of the removal reaction is 0.000312 and 0.0000568 s^{-1} for NiMo and Y-zeolite, respectively.

Table 6
Tested model equations and the assumption made

Model	Assumptions	Benzene rate equation
A	Benzene single-site adsorption rds	$-r_{1,A} = \frac{k_1 C_{bz}}{1+K_{H_2} C_{H_2} + K_{H_2O} C_{H_2O}}$
B	Benzene dual-site adsorption	$-r_{1,B} = \frac{k_1 C_{bz}}{(1+K_{H_2} C_{H_2} + K_{H_2O} C_{H_2O})^2}$
C	Benzene reaction from the gas phase	$-r_{1,C} = \frac{k_1 C_{bz} K_{H_2O} C_{H_2O}}{1+K_{H_2} C_{H_2} + K_{H_2O} C_{H_2O}}$
D	Benzene ring break-up rds	$-r_{1,C} = \frac{k_1 C_{bz} C_{bz}}{1+K_{H_2} C_{H_2} + K_{H_2O} C_{H_2O} + k_{bz} C_{bz}}$

4.2.2. Real tar model

Azner et al. [35] studied real tar steam-reforming by eight different commercial catalysts, nickel-based, which were manufactured by BASF AG, ICI-Katalco, UCI, and Haldor Topsøe a/s. The catalysts were tested in a slip flow after a biomass gasifier of fluidized bed type at small pilot-plant scale (10–20 kg of biomass/h). The gasifying agent used is steam–oxygen mixtures. All catalysts for reforming of tar show to be very active and useful for tar removal and gas conditioning (in biomass gasification). 98% tar removal is easily obtained with space velocities of 14,000 h^{-1} (n.c.). No catalysts deactivation is found in 48 h-on-stream tests when the catalyst temperature is relatively high (780–830 °C). Using a simple first-order kinetic model for the overall tar removal reaction, apparent energies of activation (of around 58 kJ/mol) and pre-exponential factors are obtained for the most active catalysts.

Narvaez et al. [36] studied raw gas from a biomass gasifier with the commercial steam-reforming BASF G1-25 S nickel-based catalyst. It is located downstream of the gasifier, a bubbling fluidized bed type in which air is used as gasifying agent. To increase the catalyst lifetime, a guard bed of a calcined dolomite at 800–850 °C is used. It decreases the through put of tar entering the catalytic bed to amounts below 2 g tar/m^3(NC). This work is focused only on the catalytic bed which easily decreases the tar content in the gas to only 1–2 mg/m^3(NC). Variables studied include the particle diameter of the catalyst, time-on-stream, temperature of the catalytic bed, and gas and tar compositions. Both tar and gas compositions in the catalytic (Ni) reactor depend on the equivalence and H/C ratios existing in the gasifier and on the operating conditions of the guard bed of dolomite. A simple kinetic model is used to describe the overall tar elimination network. Its overall kinetic constant is used as index of the catalyst activity for tar elimination. Values of this overall kinetic constant are given for very different operating conditions and shown in Table 7.

Delgado et al. [37] studied the upgrading of the raw hot gas from a bubbling fluidized bed biomass gasifier using cheap calcined minerals or rocks downstream from the gasifier. Biomass gasification is made with steam (not air) at 750–780 °C and about 0.5–1.0 kg of biomass/h. Calcined solids used are dolomite (MgO–CaO), pure calcite (CaO), and pure magnesite (MgO). Variables studied have been temperature of

Table 7
Values for the apparent activation energy and pre-exponential factor for the overall tar removal reaction

	Commercial nickel-based catalyst (tar generated in a gasifier with air)	Over a calcined dolomite (tar generated in a gasifier with steam (Delgado et al. [37]))	Tar generated in a gasifier with air (Narvaez et al., 1996; [36])
E_{app}.(kJ mol^{-1})	72 ± 12	84 ± 6	97 ± 14
k_{app}.(m^3(NC) dry/(kg/h))	143,000	2600 ± 700	$(1.2–1.4) \times 10^6$

the secondary bed (780–910 °C), time of contact or space-time of the gas (0.08–0.32 kg h/m^3 n), and particle diameter (1–4 mm) and type of mineral. Their effects on tar conversion, tar amount in the exit gas, product distribution, and gas composition are presented. Using a macro-kinetic model for the tar disappearance network, the activities of the stones are expressed by their apparent kinetic constant. Apparent energies of activation for tar elimination (42–47 kJ/mol) and pre-exponential and effectiveness factors are given for all tested solids of which the most active is the calcined dolomite.

Lv et al. [38] studied the biomass gasification by two kinds of catalysts: dolomite and nickel-based catalyst. Using a simple first-order kinetic model for the overall tar removal reaction, the apparent activation energies and pre-exponential factors are obtained for nickel-based catalysts. The E and A values are 51 kJ/mol and 14,476 (m^3 ($T_{b,wet}$)/kg h), respectively.

Bain et al. [39] did a lot of work tar reforming process using an alkali-promoted Ni-based/Al_2O_3 catalyst. A slipstream from this process was introduced into a bench-scale 5.25 cm diameter fluidized-bed catalyst reactor charged with. Catalyst conversion tests were performed at a constant space-time and five temperatures from 775 to 875 °C. The initial catalyst-reforming activity for all measured components (benzene, toluene, naphthalene, and total tars) except light hydrocarbons was 100%. The residual steady-state conversion of tar ranged from 96.6% at 875 °C to 70.5% at 775 °C. Residual steady-state conversions at 875 °C for benzene and methane were 81% and 32%, respectively. Activation energies were determined for first-order reforming reactions and catalyst deactivation. For reforming, the representative activation energies were 32 kJ/g mol for ethane, 19 kJ/g mol for tars, 45 kJ/g mol for tars plus benzene, and 8–9 kJ/g mol for benzene and toluene. For catalyst deactivation, representative activation energies were 146 kJ/g mol for ethane, 121 kJ/g mol for tars plus benzene, 74 kJ/g mol for benzene, and 19 kJ/g mol for total tars.

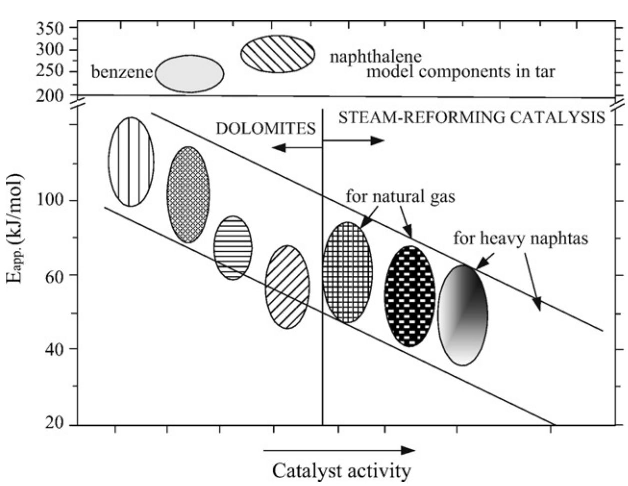


Fig. 10. E_{app} values for first-order reaction of tar elimination over calcined dolomites and steam-reforming (nickel-based) catalysts.

In brief, k_{app} defined by the whole tar should depend only on the bed temperature and gas composition, which for catalytic tar elimination has been calculated by several authors at different temperatures and for different catalysts. With the use of the Arrhenius equation, the apparent activation energy (for the first-order kinetic approach), E_{app}, was further calculated. E_{app} values found by several authors with several catalysts are summarized and shown in Fig. 10 by Corella et al. [40,41]. It is a well known fact that (for the same reaction) the apparent activation energy decreases with increasing catalyst activity. This principle has been confirmed in the tar elimination reaction, an improvement in catalyst activity resulted in a lower value for E_{app}.

5. Remarks and conclusions

- Tar chemical and physical properties are the key issue and basic for a tar successful control and convert, and the application of biomass-derived producer gas. But until now, this research field could not provide the enough data yet, so from structure-property analysis, and QSPR and molecular knowledge will benefit the solution.
- For the tar reforming mechanism, most research simplify the tar elimination reactions mechanism by two way, one is only selecting model compounds such as toluene, naphthalene, etc., representing tar mixture, this method is more easy way and accepted by most researchers; another method, catalytic tar removal is considered as a single reaction in which all tar components are regarded just only one group (tar mixture) and assumed to disappear by several simultaneous reactions of (steam-, dry-, hydro-, thermal-, ...) reforming, cracking, etc.

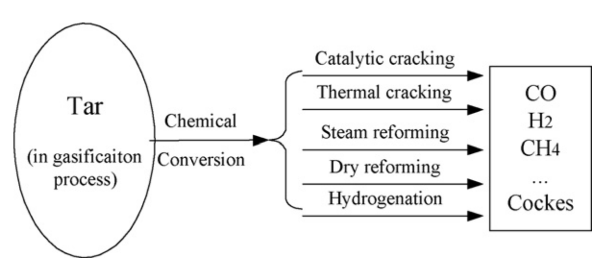


Fig. 11. One-lump model used to date for tar elimination from biomass gasification.

- A simplified reaction network for the tar catalytic removal is shown in Fig. 11. In such a simple reaction network, all tar components were grouped in just one lump and assumed to disappear by several simultaneous reactions of steam-, dry-, hydro-, thermal-reforming, cracking, etc. The overall rate of tar disappearance was thus given by the sum of the rates of all of the elementary individual reactions involved in the network. Nevertheless, going deeper into catalytic tar removal, problems soon started to appear indicating that the single, first-order reaction approach was not good enough in many ways, such as the explanation of tar reforming mechanism. But: (a) until now few research focus on the mechanism and modeling of real tar even if one model component reforming. (b) Only one model component could not indicate the real reaction rules, not reflect the interaction of the tar components.

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